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Growth and Breakdown of Surface Films and Localized Corrosion of Aluminum in Concentrated Chloride Media

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INTRODUCTION

Oxide films and salt films form on metal surfaces during anodic dissolution. In high chloride concentration environments the oxide films break down and salt films form. A number of investigations by Beck [1-9] and Isaacs and his co-workers [10-12] and others [13-18] have been directed to the elucidation of the role that salt films play in localized corrosion of metals and in mass transport of the active species that contribute to the formation and breakdown of these surface films.

Current/potential fluctuations or oscillations have been observed and related to localized corrosion [19-30]. These fluctuations have often been associated with depassivation and repassivation events involved in pitting. This erratic temporal behavior had been considered by many to occur randomly. As a result, current fluctuations have been analyzed by stochastic methods (see reviews, refs. 30, 31).

Oscillating behavior during anodic dissolution of metals have been reported for over a century (see references in ref. 32). Oscillations in potential or current have been associated with the instability of the anodic oxide and salt films formed during anodic dissolution of metals.

Oscillatory behavior was first observed in our UCLA Electrochemical Laboratory during H. C. Kuo's studies of high rate iron electrodisolution in concentrated chloride solutions in 1972 [33]. Temporal formation and disappearance of black surface films were visually observed to occur in concert with potential oscillations. The black salt film was identified as FeCl_2 [13].

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Hudson and co-workers at the University of Virginia [34,35] and investigators in the UCLA Electrochemical Laboratory [36,37] and others [38,39] have recently begun to apply nonlinear dynamic analysis to the potential/current oscillations observed during anodic dissolution of metals. With more extensive studies the results of these analyses may provide new insights into the role of salt films on localized corrosion processes such as pitting and stress corrosion cracking.

Our overall goal is to ascertain the relationships between pitting and crack initiation, the formation and breakdown of salt films (including oxides) and mechanical stress for aluminum and titanium alloys in aggressive corrosion environments. This report presents results of some very preliminary experiments on aluminum alloys and titanium during anodic dissolution in chloride media. With more extensive studies, we seek to determine if nonlinear dynamic techniques can provide further information regarding the relationship between the fluctuations and oscillations observed during anodic metal dissolution and localized corrosion phenomena.

EXPERIMENTAL

The electrochemical studies have been performed with a rotating disk electrode system. The schematic diagram of the electrochemical cell (2 liter beaker), its components, the associated instrumentation and electrode assembly has been given elsewhere [40]. The disk electrodes were prepared from alloy rods of 0.635 cm (0.25 in) diameter. The surface of each disk electrode to be exposed to the electrolyte was polished after being embedded in a Teflon cylinder with waterproof alumina paper of various grit sizes (200, 400 and 600), polished on a polishing wheel using one micron alumina powder, washed thoroughly with distilled water, degreased with acetone and finally rinsed in distilled water before being immersed in the solution.

The aluminum alloys selected for study were 6061T5 (97.9% Al, 1% Mg, 0.6% Si, 0.3% Cu, 0.2% Cr) and 2024T4 (93.5% Al, 4.4% Cu, 1.5% Mg, 0.6% Mn). The reference electrode was a saturated calomel electrode. The solutions (0.1, 1.0 and 5.0 M) were prepared from distilled water and reagent grade sodium chloride. All experiments were conducted at room temperature.

The polarization experiments were carried out with a PAR potentiostat/galvanostat (model 273). Data acquisition was performed with a PC using GPIB interface card.

RESULTS AND DISCUSSION

A series of experiments were performed with the 6061 alloy in 5 M NaCl. Figure 1 shows a current sweep at 50 mA/s when the alloy disk was rotated at 500 rpm. Potential fluctuations were observed and examination of the surfaces by an optical microscope shows considerable pit formation. Time series of the potential oscillations, power spectra and phase portraits for stationary 6061 alloy disks in 5 M NaCl at constant applied currents of 1, 5 and 50 mA are compared in Fig. 2. The amplitudes of the potential oscillations increased somewhat when the current increased from 1 to 5 mA. However, when the applied current is increased to 50 mA, the amplitudes increased by over an order of magnitude. At 1 and 5 mA, tangled trajectories in the phase portraits are seen with a higher density of the trajectories obtained at the higher current. These results indicate the

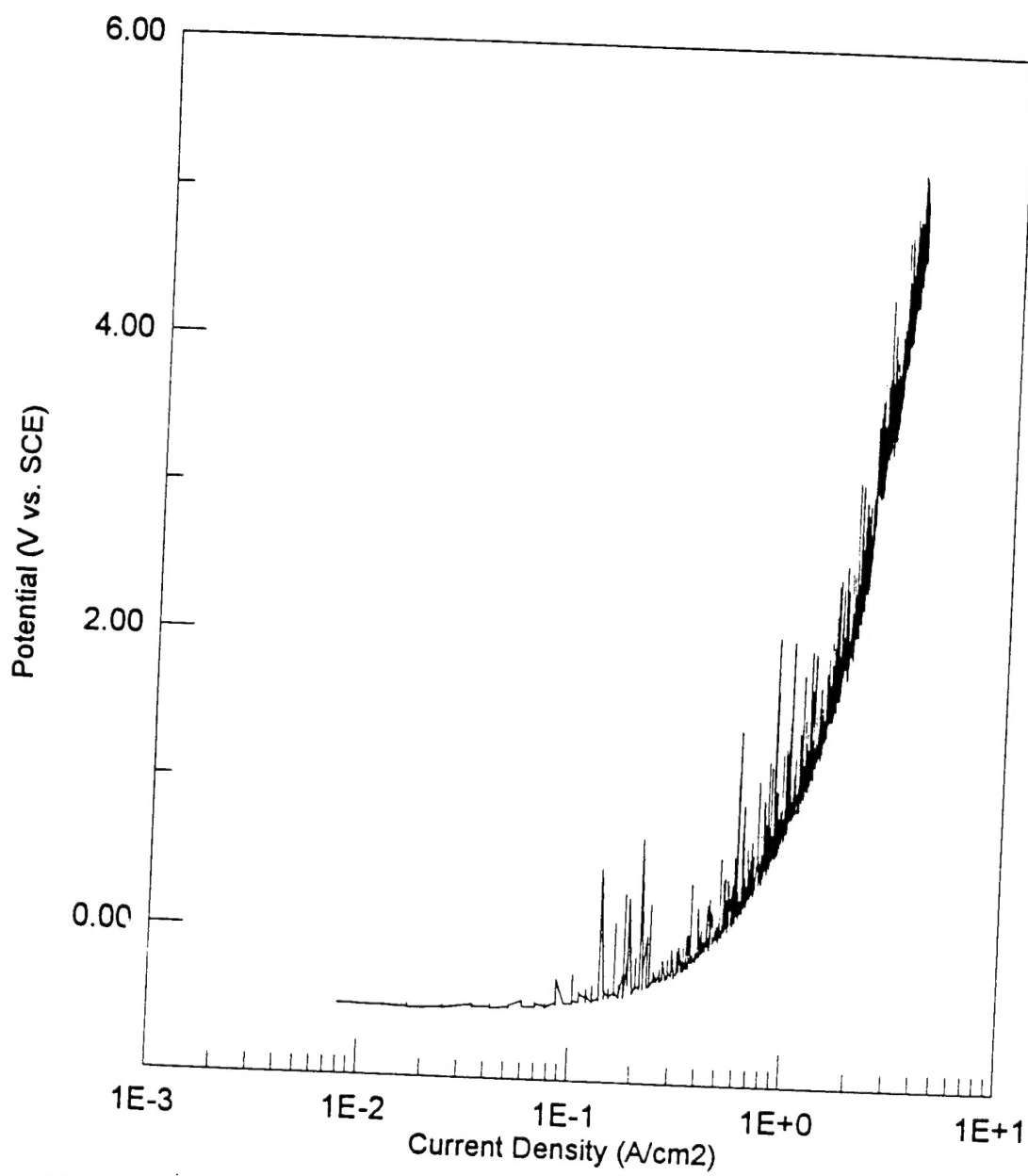


Fig 1. 6061 aluminum in 5M NaCl and 500 rpm with current sweep rate of 50 mA/sec.

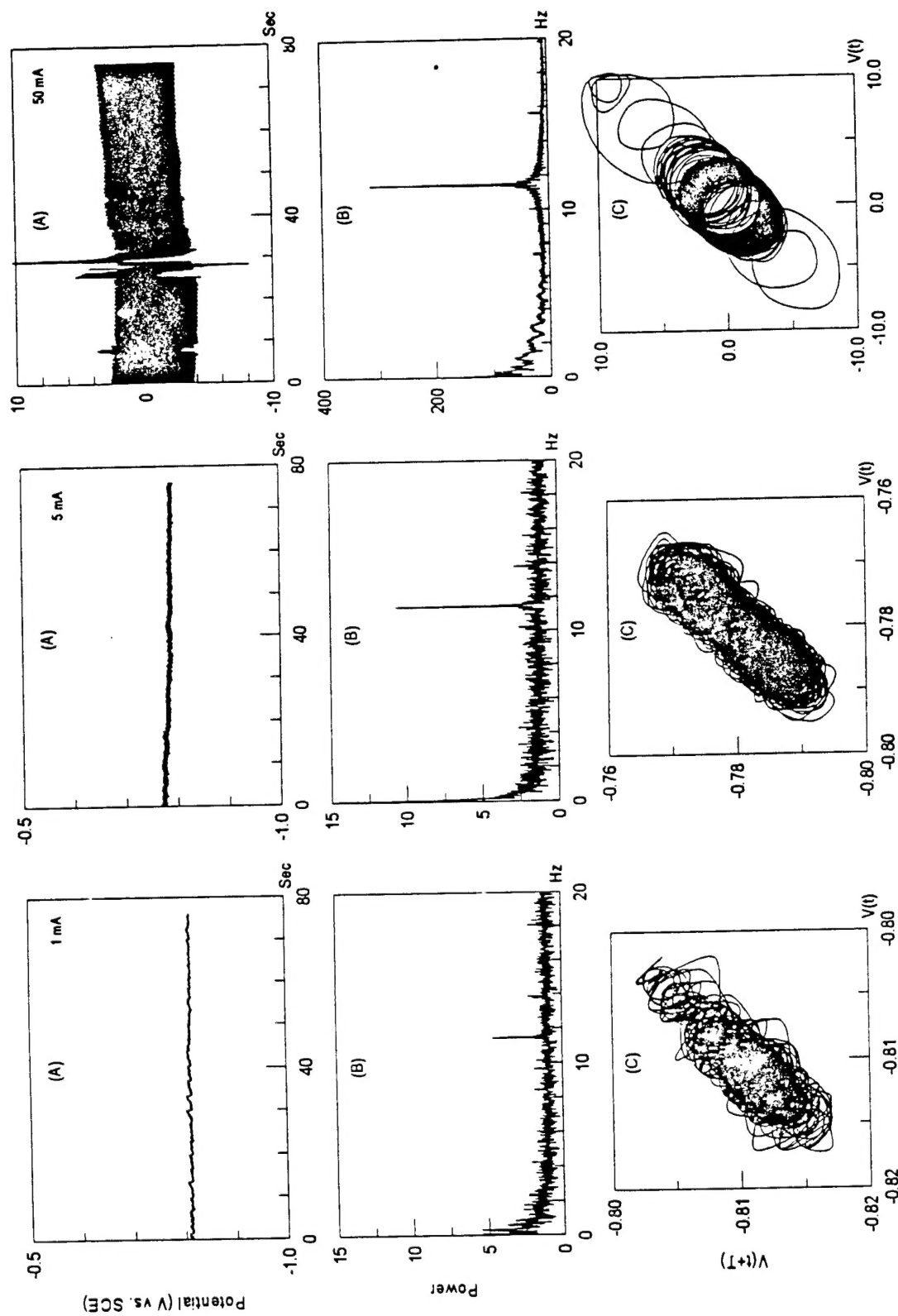


Fig. 2. 6061 aluminum in 5M NaCl with applied constant current, (A) time series, (B) power spectra, (C) phase portrait.

deterministic nature of the aperiodic potential oscillations. On the other hand, at 50 mA, a more regular appearing attractor suggests quasi-periodicity in the oscillatory behavior.

Figure 3 shows the potential sweep behavior of the 2024 alloy in 0.1, 1.0 and 5 M NaCl at rotation rates of 0, 500 and 1000 rpm. At 5 M NaCl and 100 rpm, the current fluctuations were larger at potentials near the corrosion potential. As the potential increased and approached 0.0 V vs. SCE, the current oscillations decreased. At 1 M NaCl and 1000 rpm the current fluctuations were less than observed for 5 M. It is also seen that during the potential sweep the currents decreased substantially as the rotation rates increased to 5 M. In comparison, in 0.1 M NaCl there was a small increase in currents when the rotation rates increased. By comparing the potential sweeps of the 2024 alloy in 1 M and 5 M NaCl at 1000 rpm the currents were significantly less in the higher concentration. This observation is similar to that reported during iron electrodisolution in concentrated chloride solutions and had been attributed to the change in solubility of FeCl_2 in NaCl [41]. The potential-current density behavior has been magnified between 0.7 to 0.9 V vs. SCE to enable a more detailed examination of the current fluctuations and their dependence on the chloride concentration and hydrodynamic conditions (Fig. 4).

Potential oscillations of the 2024 alloy in 0.1 M NaCl during constant current experiments of 0.0001, 1.0 and 100 mA at 500 and 1000 rpm for the first two seconds are shown in Fig. 5. An increase in rotation rate decreased the mean potential of the oscillation amplitudes. The potential oscillations at 1 mA during the first 120 seconds are shown in Fig. 5. The power spectra and the phase portraits corresponding to the time series at both 500 and 1000 rpm are also shown. Major differences in the power spectra and portraits were not evident at the two rotation rates.

Figure 6 compares the time series (first five seconds) of the potential oscillations of the 2024 alloy in 1 M NaCl during constant current experiments of 1 and 100 mA for stationary disks. In addition, a comparison of the time series (first 120 seconds) of the potential oscillations, the power spectra and phase portraits at 1 and 100 mA are shown in Fig. 6. Significant differences in all three sequences at the two currents are clearly evident.

The surfaces of the 2024 alloy after the constant current experiments were examined by optical microscopy. The density of the pits increased substantially as the chloride concentration increased from 0.1, 1.0 and 5 M NaCl. The size of the pits appeared larger for the alloy exposed to 0.1 M NaCl than either 1.0 and 5 M NaCl. Additional experiments are required to more conclusively determine the dependence of the surface morphology on the magnitude of the applied current and hydrodynamic conditions.

Some preliminary results of the oscillatory behavior of titanium (65 A) in 1 M HCl are shown in Fig. 7. The aperiodic potential oscillations, power spectra and phase portraits during constant current (1.047 A/cm^2) anodic dissolution of titanium in 1 M HCl suggest that the observed oscillations correspond to deterministic chaos rather than to random noise. Additional experiments and further analyses are needed to establish the validity of this preliminary assessment.

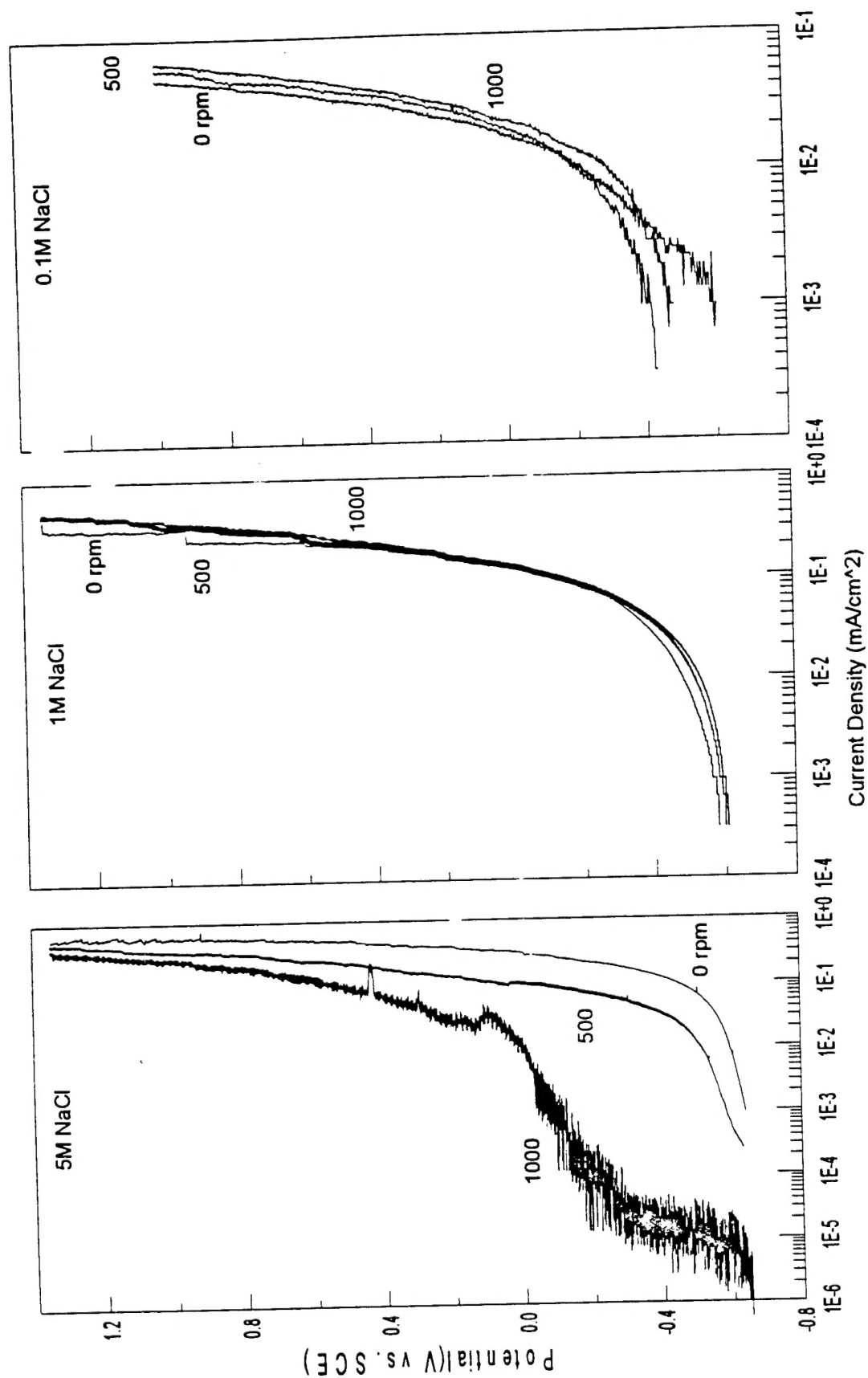


Fig 3. Potentia' sweep performed on 2024T4 aluminum. (sweep rate=10mV/sec)

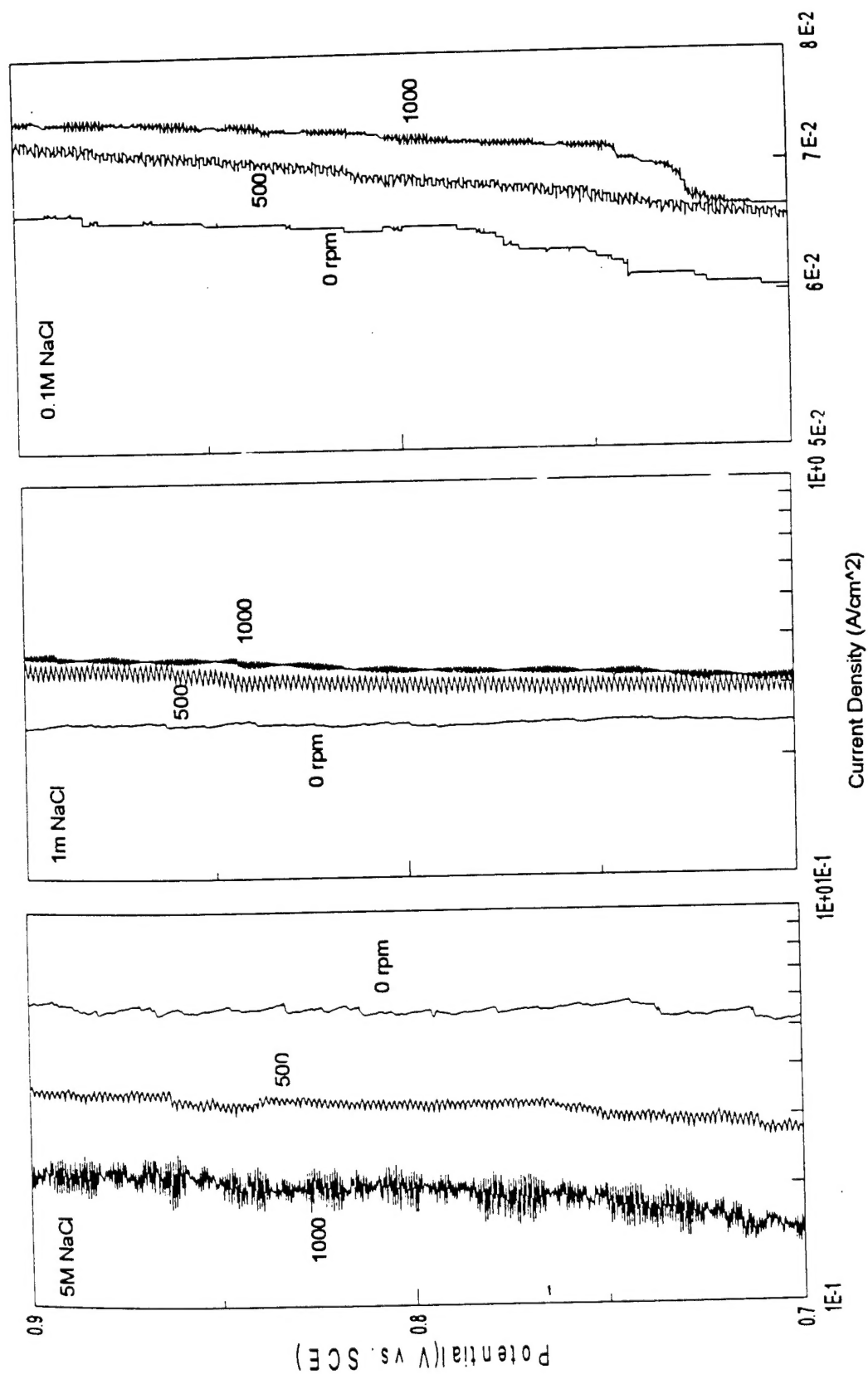


Fig 4. Potential sweep performed on 2024T4 aluminum. (sweep rate=10mV/sec)

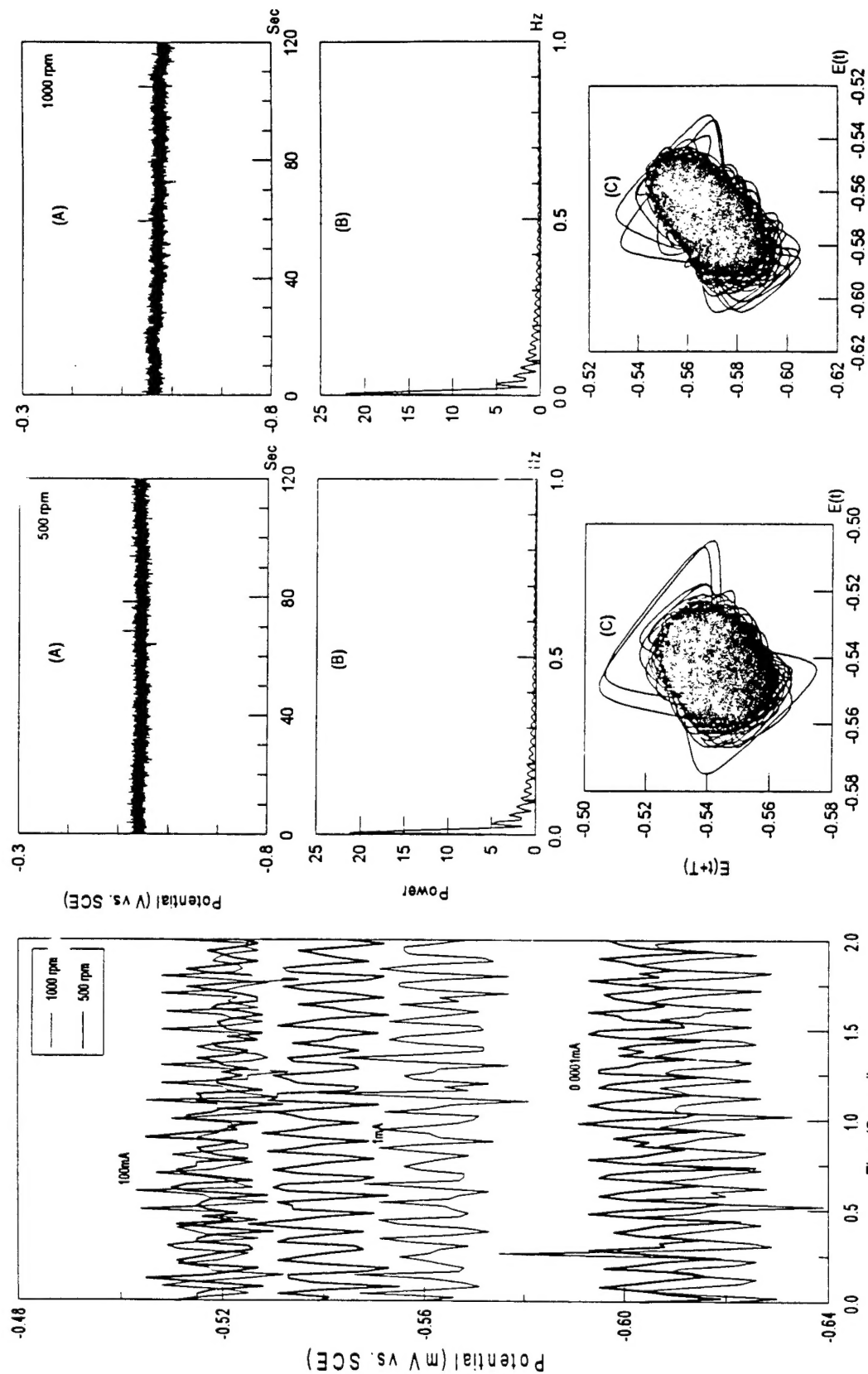


Fig 5. 2024 aluminum in 0.1M NaCl with applied constant current 1 mA
(A) time series, (B) power spectra, (C) phase portrait.

2024 aluminum in 0.1M NaCl, Time series.
(sampling rate = 0.02 sec/pt.)

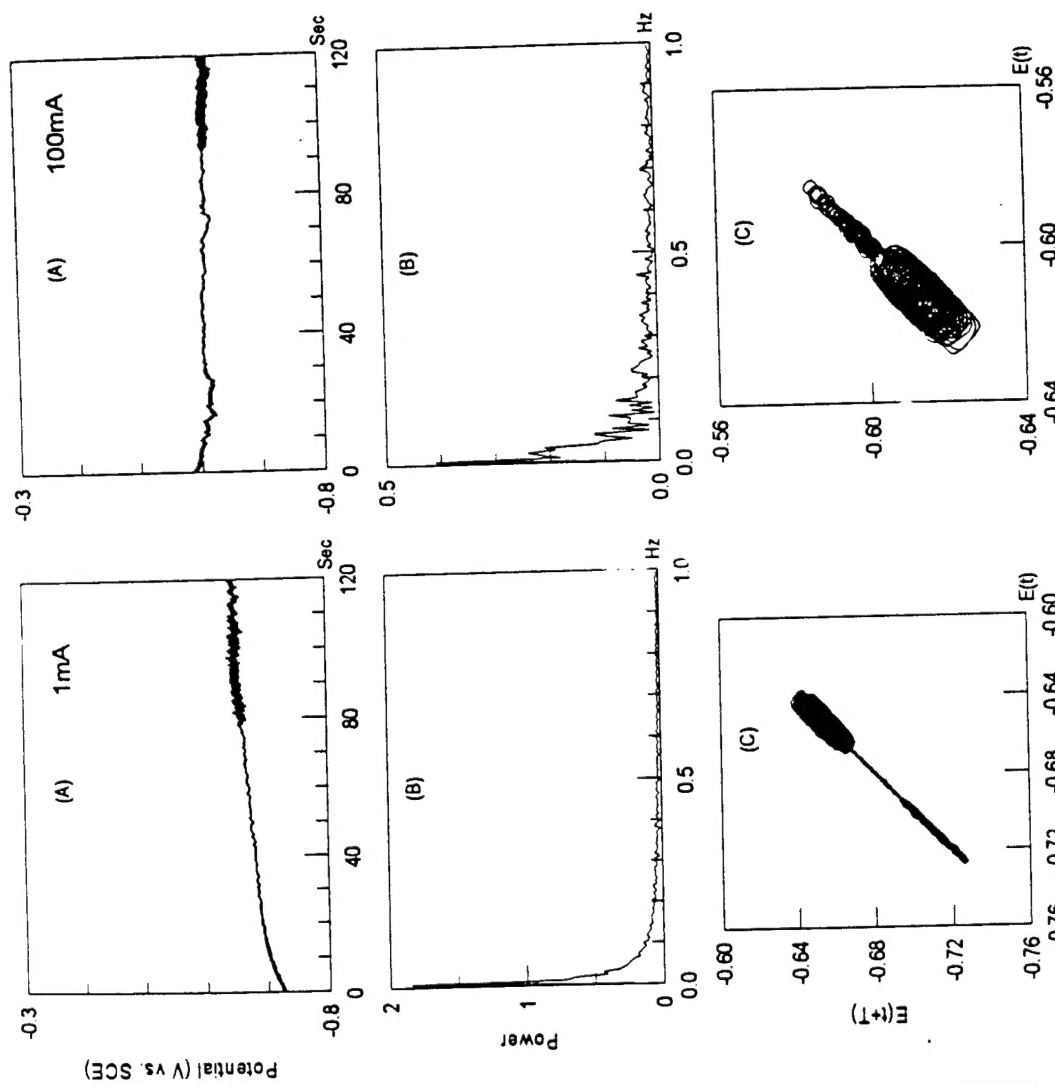
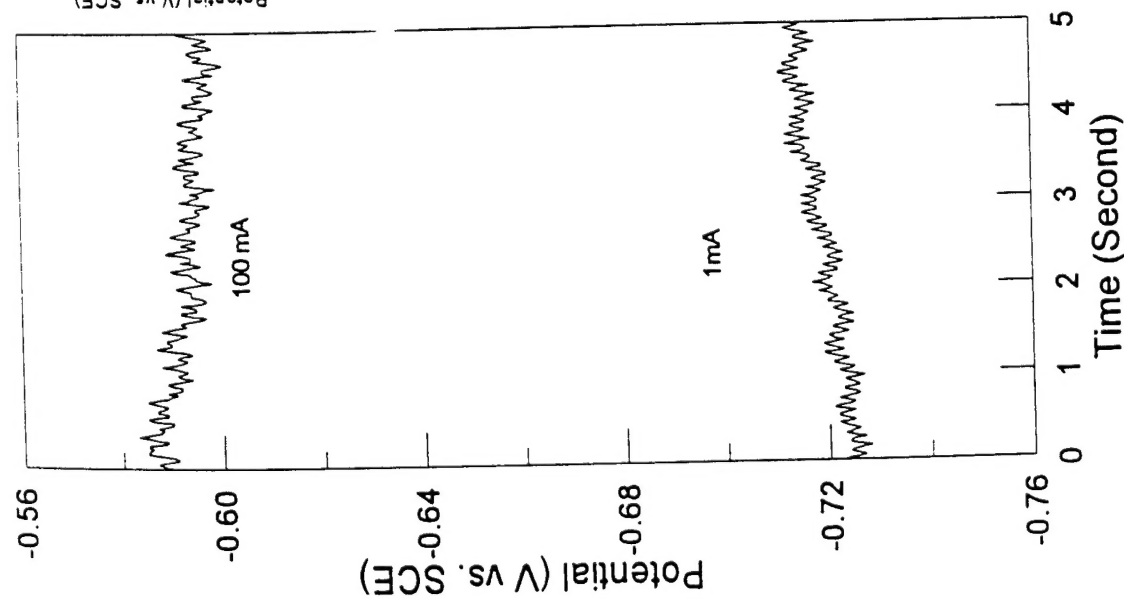


Fig 6. 2024 aluminum in 1 M NaCl with applied constant current, (A) time series, (B) power spectra, (C) phase portrait

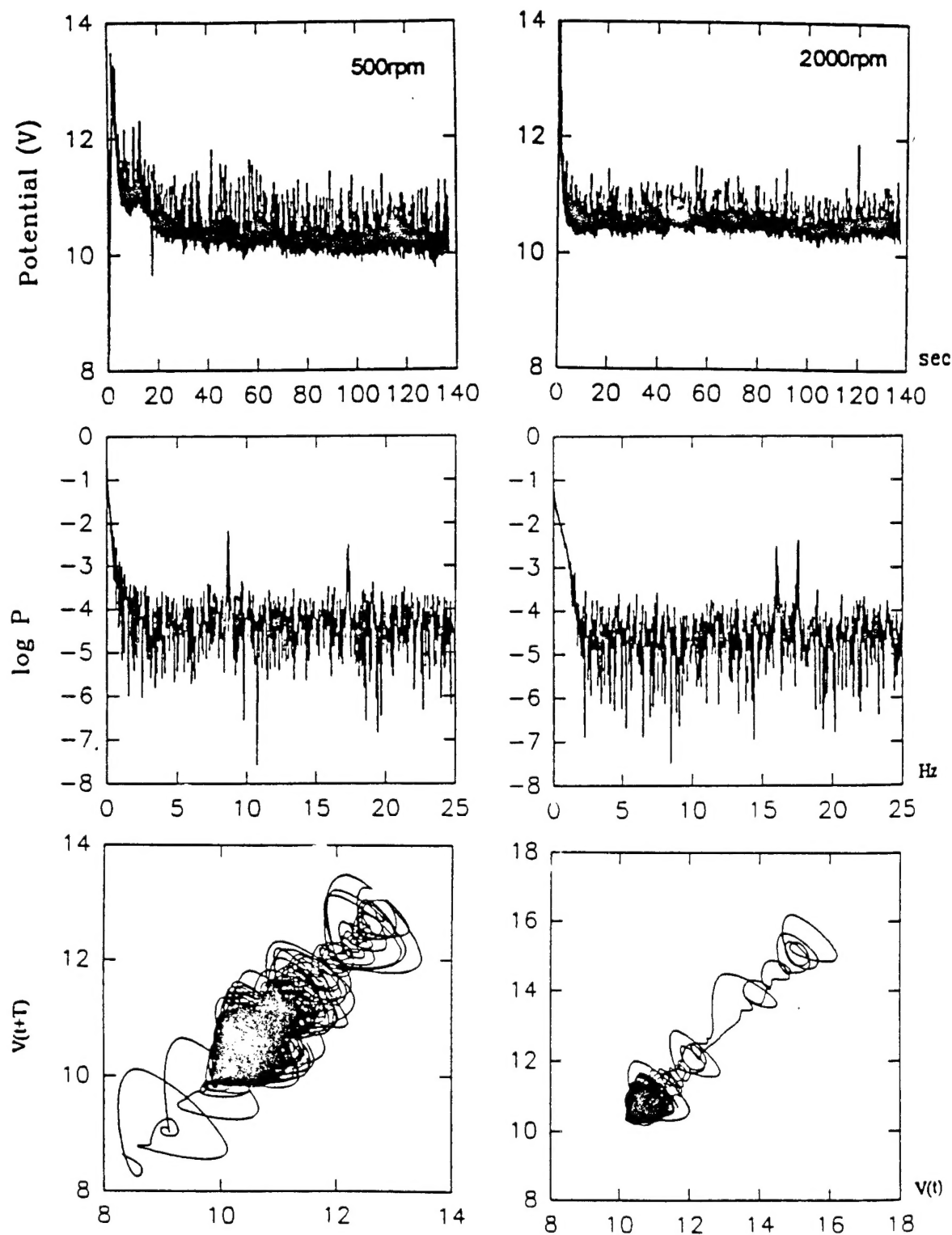


Fig 7. Titanium rotating disk electrode in 1 M HCl, 1.047A/cm²

SUMMARY OF PRELIMINARY RESULTS

Fluctuations or oscillations of potential/current were observed during preliminary anodic dissolution experiments of 6061 and 2024 aluminum alloys, and pure titanium in chloride media.

Characterization of the time series in the potential oscillations by power spectra and phase portraits suggests that the erratic temporal behavior is associated with a deterministic strange attractor and is not driven by external noise. However, further analysis is required to establish this preliminary assessment.

Examination of the surface after anodic dissolution of 2024 alloy disks by optical microscopy indicate that the density of pits increased substantially as the chloride ion concentration increased from 0.1, 1.0 to 5.0 M. Pits were larger when the alloy was exposed to 0.1 than to either 1.0 or 5.0 M NaCl.

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